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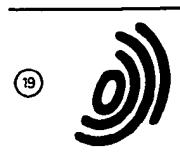
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⑳ Polyamide compositions and sealant formulations comprising them.

㉑ Alkyl- or aryl-terminated polyamide compositions and polyamide rheological additives that function as a sag/slump control agent and provide superior shear-thinning and viscosity recovery properties in systems that react with or are sensitive to water or other active hydrogen containing materials and systems that do not react with or are not sensitive to water or other active hydrogen containing materials, and are useful in sealants, caulk, adhesives and coatings, are obtained by reacting

- 1) polycarboxylic acids with monoamines,
- 2) polycarboxylic acids with both mono- and polyamines,
- 3) polyamines with monocarboxylic acids, or
- 4) polyamines with both mono- and polycarboxylic acids.

In an example, a mixture of dimerized fatty acids and sebacic acid is reacted with octadecylamine. The amide product is used in polyurethane sealant formulations.

EP 0 467 533 A1

The present invention relates to alkyl- and aryl-terminated polyamide compositions that function as rheological additives, including sag/slump control agents, when incorporated into sealant, caulk, adhesive and coating formulations, and provide superior shear-thinning and viscosity recovery properties.

Rheological additives have been widely employed in the formulation of products such as sealants, 5 adhesives and coatings to provide control of sag or slump during and after application. Various organic and inorganic materials such as fumed silicas, carbon blacks, asbestos, castor oil derivatives, organomodified clays, and other minerals, fibres and organic synthetics, such as polyurethanes and polyamides, have provided thixotropic properties to end products, particularly non-reactive products.

US-A-4778843 discloses polyamide rheological additives wherein the polyamide chain is capped with a 10 monocarboxylic acid having from 16 to 22 carbon atoms, and with either olefinic unsaturation or a hydroxyl group, which have been found to be effective in thickening non-reactive organic solvent based coating systems.

US-A-4670173 discloses oil-soluble compositions that are useful as viscosity modifiers. Such compositions are formed by reacting an acylating product, a polyamine and a mono-functional acid, either in the 15 presence of a hydrocarbon solvent or in the absence of a solvent.

US-A-4462926 discloses a polyamide thixotrope for unsaturated polyester resins consisting of at least one cyclohexyl amide of a saturated fatty acid which contains at least 10 carbon atoms and at least one oligomeric ester amide having an average molecular weight of 600 to 3000, a content of carboxylic acid amide groups of 1.5 to 15% by weight and a content of carboxylate groups of 2 to 13% by weight.

EP-A-0392171 (90103360.5) describes polyamides of one type shown in the specification for use as encapsulants for curing agents for reactive hot melt adhesives.

In many systems, however, either the basic components show appreciable reactivity towards such conventional rheological additives, or the additives are simply impractical because of inferior performance, cost, or undesirable side effects. One such system is the one component moisture-cured polyurethane 25 sealants. Such sealants are based on urethane prepolymers with reactive isocyanate functionality. The isocyanate groups of these molecules react readily with active hydrogen containing species such as water, primary and secondary amines, and compounds with hydroxyl carboxyl or mercaptan groups. Many of the conventional rheological additives, such as fumed silicas, castor oil derivatives and organomodified clays, contain one or more types of these active hydrogen groups, and therefore cause detrimental effects to the 30 sealant, such as interference with cure rate, final physical properties or package stability. Additionally, the additives are often rendered inactive due to consumption of active hydrogen groups by the isocyanate groups of the urethane prepolymer.

Some existing rheological additives are relatively inert towards isocyanates if dried and employed under anhydrous conditions, but their use is limited by other factors. For example, the use of asbestos has been 35 essentially eliminated because of its carcinogenicity. Fine particle/high structure carbon blacks are only effective at high concentrations, and also make the sealant black in colour. Further, various organic fibres are either high in cost, low in efficiency or lead to undesirable appearance of the sealant product.

Other products or techniques have been employed, such as PVC plastisol fusion, but such processes are very process-sensitive or labour intensive.

Polyamides of certain types have been shown to impart thixotropy in various resin or solvent systems. 40 However, polyamides typically possess active hydrogen functionality, such as in amine or carboxylic acid groups. As set forth in US-A-4778843, recently introduced polyamide rheology modifying agents have hydroxyl functionality. Such active hydrogen-containing species react with isocyanates, resulting in final product instability, cure impediment, rheology deactivation or other detrimental effects.

A need exists in the art for a rheological additive that overcomes the foregoing shortcomings.

The present invention overcomes the problems and disadvantages of the prior art by providing alkyl- and aryl-terminated non-reactive polyamide rheological additives that exhibit superior properties over prior art rheological additives when incorporated into sealants, caulk, adhesives and coatings.

It is an object of the present invention to provide polyamide rheological additives that do not contain 50 appreciable levels of active hydrogen-containing species.

It is a further object of the invention to provide polyamide rheological additives that can be easily incorporated into, and are compatible with, sealant, caulk, adhesive and coating formulations.

It is an additional object of the invention to provide polyamide rheological additives that provide shear-thinning characteristics, ie, high viscosity at low shear rates and low viscosity at high shear rates in systems 55 in which the polyamide rheological additives are incorporated. A measure of this property is the thixotropic index, TI, where

$$\frac{\text{TI} = \text{Viscosity at shear rate 1}}{\text{Viscosity at shear rate 2}}$$

5

and shear rate 1 is less than shear rate 2.

It is yet a further object of the invention to provide polyamide rheological additives that exhibit recovery of initial viscosity immediately after application of shear to the end use system.

10 The present invention provides alkyl- and aryl- terminated polyamide rheological additives useful in sealant, caulk, adhesive and coating formulations. The polyamide rheological additives are prepared by one or more of the following reactions (1) - (4):

**Reaction (1):** reacting at least one polycarboxylic acid of the formula

15 (A)[COOH]<sub>x</sub> (I)

wherein x is at least 2 and A is an x-valent aliphatic, aromatic, cycloaliphatic or arylaliphatic group, with at least one monoamine of the formula

20 (G)NH (II)

wherein G is an aliphatic, aromatic, cycloaliphatic or arylaliphatic group, and wherein the monoamine may include primary amines and/or secondary amines, and when the monoamine contains a primary amine, the additional hydrogen atom is included in the (G) moiety, whereby to form a polyamide of the formula

(G)NOC(A)CON(G) (a)

30 **Reaction (2):** reacting at least one polycarboxylic acid of the formula (I) with at least one monoamine of the formula (II), and at least one polyamine of the formula

35 (D)[NH]<sub>y</sub> (III)

wherein y is at least 2 and D is a y-valent aliphatic, aromatic, cycloaliphatic or arylaliphatic group, and wherein the polyamine may include primary amines and/or secondary amines, and when the polyamine contains a primary amine, the additional hydrogen atom is included in the (D) moiety, whereby to form a polyamide of the formula

40 (G)NOC(A)CO[N(D)NOC(A)CO]<sub>n</sub>N(G) (b)

wherein n is from 1 to infinity.

**Reaction (3):** reacting at least one polyamine of the formula (III) with at least one monocarboxylic acid of the formula

(E)COOH (IV)

50 wherein E is an aliphatic, aromatic, cycloaliphatic or arylaliphatic group, whereby to form a polyamide of the formula

(E)CON(D)NOC(E) (c)

55 **R action (4):** reacting at least one polycarboxylic acid of the formula (I) with at least one polyamine of the formula (III) and, at least one monocarboxylic acid of the formula (IV) whereby to form a polyamide of the formula



wherein n is from 1 to infinity.

The polyamide rheological additives of the invention may also be prepared by reacting to form mixtures of any of the reaction products formed from any of above reactions (1) - (4).

The formulas of polycarboxylic acids and polyamines set forth above only include those with a functionality of two, ie, x = 2, y = 2, for illustrative convenience. Polycarboxylic acids and polyamines with a functionality of 3 or more may also be employed. Each branch point chain resulting from inclusion of such higher functionality materials will follow a similar pattern of polyamide chain structure to those illustrated above.

The above reactions may or may not be carried out in the presence of a catalyst.

As used herein, the term "polyamide" includes any of the products of the reactions (1) - (4) set forth above wherein the average number of amide linkages is at least about two.

As used herein, the term "polycarboxylic acid" includes all aliphatic or aromatic carboxylic acids having a functionality of at least two, as well as the corresponding acid anhydrides, esters and acid halides.

As used herein, the term "polyamine" includes all aliphatic or aromatic primary or secondary amines having a functionality of at least two.

As used herein, the term "monocarboxylic acid" includes all aliphatic or aromatic carboxylic acids having a functionality of one, as well as the corresponding acid anhydrides, esters and acid halides.

As used herein, the term "monoamine" includes aliphatic or aromatic primary or secondary amines having a functionality of one.

The molar quantities of the reactants of reactions (1) to (4) are whole numbers, with the exception that the number of moles of monocarboxylic acid of formula (IV), or of the monoamine of formula (II), may be a fractional quantity if the average functionality of the polyamine and/or polyacid containing backbone is fractional, since the number of moles of capping agent is equal to the functionality of the backbone.

In reaction (1), at least 2.0 moles of monoamine are employed. The number of moles of monoamine equals the average functionality of the polycarboxylic acid. 1.0 mole of polycarboxylic acid is employed.

In reaction (2), at least 2.0 moles of monoamine are employed. The number of moles of monoamine equals the average functionality of acid-terminated polyamide from the reaction of the polycarboxylic acid and the polyamine. At least 2.0 moles of polycarboxylic acid are employed, and the number of moles of polycarboxylic acid employed is the same as or more than the number of moles of polyamine employed. The number of equivalents of polycarboxylic acid is greater than or equal to the number of equivalents of polyamine plus 2.0. The number of equivalents of polycarboxylic acid minus the number of equivalents of polyamine equals the number of equivalents of monoamine.

In reaction (3), at least 2.0 moles of monocarboxylic acid are employed. The number of moles of monocarboxylic acid is equal to the average functionality of the polyamine. 1.0 mole of polyamine is employed.

In reaction (4), at least 2.0 moles of monocarboxylic acid are employed. The number of moles of monocarboxylic acid employed is equal to the average functionality of the amine-terminated polyamide from the reaction of the polyamine and the polycarboxylic acid. At least 2.0 moles of polyamine are employed. The number of moles of polyamine employed is greater than or equal to the number of moles of polycarboxylic acid employed. The number of equivalents of polyamine is greater than or equal to the number of equivalents of polycarboxylic acid plus 2.0. The number of equivalents of polyamine minus the number of equivalents of polycarboxylic acid equals the number of equivalents of monocarboxylic acid.

The polyamide rheological additives of the invention are useful in both reactive systems, i.e., systems that are reactive with or are sensitive toward water or other active hydrogen-containing materials and non-reactive systems, i.e. systems that do not react with or are not sensitive towards water or other active hydrogen-containing materials. The invention also provides reactive composites comprising a reactive system and the polyamide rheological additives of the invention. The invention further provides non-reactive composites comprising a non-reactive system and the polyamide rheological additives of the invention.

The polyamide rheological additives of the invention provide sag or slump control when incorporated into sealant, adhesive, caulk and coating formulations, and provide shear-thinning and viscosity recovery properties without impairing the properties of the end product, such as package stability and cure rate.

The polyamide rheological additives of the invention provide immediate recovery of high viscosity after cessation of shear applied to the end use product, ie, in less than ten seconds after application of the end use system containing the rheological additive to an end use substrate or assembly, the end use system returns to a non-flowable consistency. The property can be assessed by testing the end use system according to ASTM D2202 or ASTM C639. If, during evaluation by either of these two tests, the product

exhibits no pronounced sagging or slumping, the recovery is considered immediate.

The polyamide rheological additives of the invention may be prepared as a free-flowing powder or, in combination with a solvent or plasticizer, as a paste. Further, the polyamide rheological additives are effective at low use levels of from 0.5 to 5 weight percent loading (the weight percentage being based on the total weight of the end use system), depending upon the type of system employed.

Reference will now be made in detail to the present preferred embodiments of the invention.

Exemplary suitable polycarboxylic acids for use in the invention include dimerized and trimerized fatty acids. As used herein the term "dimerized fatty acids" includes any acid obtained by dimerizing saturated, ethylenically unsaturated or acetylenically unsaturated, naturally occurring or synthetic, monobasic aliphatic carboxylic acids containing from 8 to 24 carbon atoms, 18 carbon atoms being quite common. Such dimerized fatty acids comprise a mixture of about 36 carbon atom dicarboxylic acids and usually also contain several isomeric dimers, together with a small amount of trimer and higher polymers, and are fully described in US-A-4018733 and Empol Dimer and Polybasic Acids, A-2026, Emery Chemicals, Cincinnati, Ohio.

As used herein, the term "trimerized fatty acid" includes any acid obtained by trimerizing saturated, ethylenically unsaturated or acetylenically unsaturated, naturally occurring or synthetic, monobasic aliphatic carboxylic acids containing from 8 to 24 carbon atoms. Such trimerized fatty acids comprise a mixture of about 54 carbon atom tricarboxylic acids, and usually also contain several isomeric trimers together with a small amount of dimers, tetramers and higher polymers.

Additional exemplary suitable polycarboxylic acids include oxalic acid, glutaric acid, malonic acid, adipic acid, succinic acid, suberic acid, sebacic acid, azelaic acid, dodecanedioic acid, pimelic acid, terephthalic acid, isophthalic acid, phthalic acid, naphthalene dicarboxylic acids, and 1,4- or 1,3-cyclohexane dicarboxylic acids.

In general, any polycarboxylic acid in which the carboxylic acid groups are separated by a divalent hydrocarbon group, which may be saturated or unsaturated, aliphatic, aromatic or cycloaliphatic, or which may have two or more aliphatic, aromatic or cycloaliphatic moieties, can be used to form the polyamides employed according the invention. Also, any polycarboxylic acid in which the average functionality (number of functional groups per molecule) is greater than two may be used. Exemplary suitable polycarboxylic acids include 1,3,5-pantanetricarboxylic acid, 1,3,3-propanetricarboxylic acid, 1,2,3,4-butanetetracarboxylic acid and trimellitic acid. Corresponding acid anhydrides such as trimellitic anhydride, esters, and acid halides of the foregoing acids are also suitable for use in the present invention.

Exemplary suitable polyamine compounds for use in the invention include ethylene diamine, 1,2-diaminopropane, 1,3-diaminopropane, 1,4-diaminobutane, p-xylene diamine, 1,6-hexamethylene diamine, 2-methylpentamethylene diamine, 4,4'-methylenebis(cyclohexylamine), 2,2-di-(4-cyclohexylamine)-propane, polyglycol diamines, isophorone diamine, m-xylene diamine, p-phenylene diamine, 1,2-diaminocyclohexane, 1,4-diaminocyclohexane, cyclohexanebis(methylamine), bis-1,4-(2'-aminoethyl)benzene, 9-aminomethylstearylamine, 10-aminoethylstearylamine, 1,3-di(4-piperidyl)propane, 1,10-diaminodecane, 1,12-diaminododecane, 1,18-diaminotadecane, piperazine, N-aminoethylpiperazine, bis-(3-aminopropyl)piperazine, polyethylene polyamines such as diethylene triamine and triethylene tetramine, diethyltoluene diamine, methylene dianiline and bis(aminoethyl)diphenyl oxide. Polymeric fat polyamines and ether polyamines may also be used. These polyamines are described in US-A-4018733 and -3010782, and the Jeffamine Polyoxyalkyleneamines, NPD-024 102-0745, Texaco Chemical Company, Bellaire, Texas.

Exemplary suitable monocarboxylic acids for use in the invention include fatty acids. The term "fatty acids" as used herein includes saturated, ethylenically unsaturated and acetylenically unsaturated, naturally occurring and synthetic monobasic aliphatic acids containing from 8 to 24 carbon atoms. Exemplary suitable saturated fatty acids include branched and straight chain acids such as caprylic acid, pelargonic acid, capric acid, lauric acid, myristic acid, palmitic acid, isopalmitic acid, stearic acid, isostearic acid, arachidic acid, behenic acid and lignoceric acid. Exemplary suitable ethylenically unsaturated acids include the branched or straight chain, poly- and monoethylenically unsaturated acids such as 3-octenoic acid, 11-dodecenoic acid, linderic acid, lauroleic acid, myristoleic acid, tsuzuic, palmitoleic acid, petroselinic acid, oleic acid, elaidic acid, vaccenic acid, gadoleic acid, cetoleic acid, nervonic acid, linoleic acid, linolenic acid, eleostearic acid, hiragonic acid, moroctic acid, timnodimic acid, eicosatetraenoic acid, nisinic acid, scoliodonic acid and chaulmoogric acid. Acetylenically unsaturated fatty acids, both straight and branched chain, both mono-unsaturated and polyunsaturated are useful herein. Exemplary suitable fatty acids include 1-undecynoic acid, taric acid, stearolic acid, behenolic acid and isamic acid. Also, monocarboxylic acids having from two to seven carbon atoms may be used, such as acetic acid, propionic acid, butyric acid, valeric acid and caproic acid.

Exemplary suitable monoamines for use in the invention include methylamine, dimethylamine,

ethylamine, diethylamine, n-propylamine, di-n-propylamine, isopropylamine, n-butylamine isobutylamine, sec-butylamine, tert-butylamine, di-n-butylamine, monoamylamine, diamylamine, ethylbutylamine, n-hexylamine, di-n-hexylamine, cyclohexylamine, benzylamine, alpha-phenylethylamine, beta-phenylethylamine, aniline, methylamiline, diphenylamine, o-toluidine, m-toluidine, p-toluidine, o-anisidine, m-anisidine, p-anisidine, dodecylamine, cocoamine, hexadecylamine, octadecylamine, oleylamine, dicocoamine, and di(hydrogenated-tallow)amine; amides such as cocoamide, octadecanimide, oleamide, o-toluene sulfonamide and p-toluene sulfonamide; and polyetheramines such as polyoxyethylene amine(s) and polyoxypropylene amines(s).

Exemplary suitable catalysts for use in the invention include acid compounds such as phosphoric acid, oxides or carbonates of an alkaline nature such as magnesium oxide or calcium oxide and halogen salts of polyvalent metals and acids. The catalyst is preferably present in an amount from 0 to 3% by weight of the reactants, more preferably in an amount from 0.005 to 0.500% by weight, most preferably in an amount of about 0.01% by weight of the reactants.

The ratio of equivalents of amine to acid groups for the polyamide rheological additive synthesis is preferably from 0.8:1.0 to 1.2:1.0 equivalents of amine to acid (NH/COOH), more preferably from 0.95:1.00 to 1.05:1.00 equivalents NH/COOH, most preferably about 1.0:1.0 equivalents NH/COOH.

As used herein "amine" or "NH" means any primary or secondary amine group. As used herein, "acid" or "COOH" represents any carboxylic acid, ester, acid halide or anhydride group.

In addition to the polyamide containing products formed in reactions (1) - (4) above, by-products may be formed. Except for minute quantities, the by-products are removed during the synthesis. The by-products formed are as follows:

carboxylic acid + amine → water  
ester + amine → alcohol  
acid halide + amine → hydrogen halide  
anhydride + 2 amines → water

Synthesis is performed in typical glass resin reaction equipment. All processing is performed under a dry nitrogen blanket or a sparge, or under vacuum, to prevent oxidative degradation from taking place. Vacuum processing is implemented particularly during the final stages of the reaction to remove minor amounts of water, air, other by-products, or volatile unreacted starting materials such as amines. Vacuum processing is preferred, although not absolutely necessary.

The reactants are blended and heated gradually to 220 - 240 °C. During temperature elevation, one or more condensers and a receiving vessel may be employed to collect the water or other by-products of reaction, as well as any volatilized starting materials. Once the reaction mass has achieved a steady state, ie, when colour appearance, and viscosity cease to change and the acid and amine values have reached a stable minimum (preferably less than 1 mg KOH/g each), full vacuum is applied (greater than 29 in Hg) for a period of one to two hours. The product is then packaged and cooled. The solid product is then milled to a free-flowing powder. It is then stored until its incorporation in a sealant, adhesive or coating formulation.

Alternative methods of preparation involve synthesizing the polyamide as described above and then diluting it in an appropriate plasticizer or solvent at either of two stages. The first stage dilution is described as follows. After the application of vacuum, the molten product is allowed to cool to a minimum temperature at which it is still liquid. Then the diluent is introduced while mixing. Once homogeneous, the diluted product can be degassed and discharged. The final cooled product may be a liquid, a paste or a solid.

The second stage dilution involves taking the 100% synthesized product through the milling and sieving process, and then dispersing the powdered product in the diluent of choice, using one of several possible methods, such as a high speed dispersator or a planetary mixer. By this method, the final product may be a liquid or a paste.

The invention will be further clarified by the following Examples. All synthesis, milling, compounding and packaging operations described in the following examples are performed under a constant dry nitrogen purge unless otherwise noted.

50

#### Example 1: Preparation of Powdered Polyamid Rheological Additive

368.7 g of Empol 1010 (dimerized fatty acids, Henkel Corp, Emery Group, Cincinnati, Ohio), 8.0 g of a mixture of 1% by weight orthophosphoric acid and 99% by weight of Empol 1010, and 15.0 g of Sebacic Acid, CP grade (Union Camp Corp, Wayne, NJ) were charged into a one litre resin reaction flask, and mixed (using an electric mixer and a dual impeller shaft) with mild heating (using a heating mantle). Once uniform, 408.2 g of Armeen 18D (octadecylamine, Akzo Chemicals, Inc, Armak Chemicals, Chicago, Illinois) were added gradually and mixed in over a 15 minute period. The reaction mixture was mixed and heated

until homogeneous with all components molten. The temperature was elevated gradually to 231 °C over a period of four hours from the time when the Armeen 18D charge was completed. During this temperature elevation, vigorous bubbling was observed due to the conversion into amide and evolution of condensed water (i.e., water formed as a by product of the reaction). The temperature was maintained above 220 °C for a period of two hours, during the final hour of which a vacuum of greater than 29 in Hg was applied. The molten liquid product was then discharged into release paper lined boxes and allowed to cool overnight in a desiccator, a hard brittle solid resulted. The solid product was then broken into small fragments and milled to a powder using a Brinkmann centrifugal mill with liquid nitrogen prechilling of the fragments. The -60 mesh (250 µm) fraction was sieved with a 60 mesh (250 µm) screen (US Standard Sieve Series, No 60 (250 micrometre opening), Tyler equivalent = 60 mesh) to remove the coarser fraction. The powder was transferred to air-tight 250 ml polypropylene jars for storage and later use. The final product was an off-white free-flowing powder.

#### Test Results:

15

	Acid Value (mg KOH/g)	0.6
	Amine Value (mg KOH/g)	1.3
	Shore D Hardness	38
20	Ring and Ball Softening Point (°C)	98
	Brookfield Thermosel Viscosity (cP) (Model RV, Spindle # SC4-27/100 rpm/120°C)	55

25

#### Example 2: Preparation of Paste Form

Using a Premier Dispersator with a 48 mm saw-toothed blade and a derimmed 500 ml can, 100.0 g PX-316 (mixed n-alkylphthalate, Aristech Chemical Corp, Pittsburgh, PA) were charged and mixed at 1000 rpm. A 100.0 g portion of the powdered polyamide from Example 1 was gradually charged over a period of six minutes. When approximately half of the powdered additive was charged, the mixer speed was increased to 2000 rpm. Once all of the powdered additive was charged, the mixer speed was increased to 5000 rpm and mixing was continued for 14 minutes, at which time a temperature of 47 °C was reached from the heat of mixing. The warm dispersion was placed in a vacuum desiccator and full vacuum (greater than 29 in Hg) was applied for 12 minutes, and then transferred to an air-tight 250 ml polypropylene jar for storage and later use. The final product was an easily workable past of off-white to yellow colour which exhibited shear-thinning and rapid recovery of viscosity.

#### Test Results:

40

Cone Penetration at 21 °C (mm) = 18.5  
(ASTM D217, Cone Penetration Test non-worked material, standard cone)

#### Example 3: Preparation of Plasticized Polyurethane Sealant Prepolymer

45

1228.8 g of Voranol 220-056 (polyoxyalkylene diol, Dow Chemical Co, Midland, Michigan) and 673.5 g of Voranol 232-034 (polyoxyalkylene triol, Dow Chemical Co, Midland, Michigan) were charged into a four litre resin reaction flask. The polyols were mixed (using an electric mixer and a three impeller shaft) and heated (using a heating mantle) to 60 °C. Then 347.4 g of molten (50 °C) Isonate 2125M (4,4'-diphenyl-methane diisocyanate, Dow Chemical Co, Midland, Michigan) were added and the contents of the reactor were mixed without heating for six minutes, after which the temperature was 59 °C. Next, 11 drops (0.31 g) of Dabco T-9 (stannous type organometallic catalyst, Air Products and Chemicals Inc, Allentown, PA) were added. Two minutes later an exotherm to 90 °C was observed. After three additional minutes (at T = 86 °C), 750.0 g of PX-316 (mixed n-alkylphthalate, Aristech) were added gradually over a four minute period, after which the temperature had dropped to 69 °C. A vacuum was gradually applied over a 23 minute period. Full vacuum (greater than 29 in Hg) was then maintained for 10 minutes. The resulting plasticized urethane prepolymer was then discharged into airtight high density polyethylene jars of 1 litre capacity for storage and later use.

### Test Results:

% NCO = 1.27  
Brookfield Viscosity (cP) = 33,000  
(Model RV, Spindle # 6/20 rpm/23°C)

#### 10 Example 4: Preparation of One-Component Moisture-Cured Polyurethane Sealant Formulation

393.8 g of plasticized prepolymer from Example 3 were charged into an 8 litre Ross double planetary mixer, then mixed at moderate speed for 10 minutes under full vacuum (greater than 29 in Hg). Then 930.0 g of BLR/3 (hydrophobically surface-treated calcium carbonate, Omya Inc, Proctor, Vermont) were added and mixed in at low speed for a sufficient time for the mixture to appear homogeneous. Then a full vacuum was applied and the mixture was blended at high speed for 17 minutes. The material was scraped from the mixing blades and container walls with a steel spatula. Then 131.7 g of plasticized prepolymer from Example 3 were added and mixed in at high speed for 10 minutes under full vacuum. Again the mixing blades and container walls were scraped. Then 45.0 g of anhydrous m-Xylene were charged and mixed in at moderate speed for 12 minutes under full vacuum. The finished sealant product was then packaged into polyethylene cartridges of 200 ml capacity which were then placed into polyethylene lined aluminum foil pouches with desiccant. The pouches were then heat-sealed for storage and subsequent evaluation. The tests and results are set forth in Table I.

## 25 Example 5: Preparation of One-Component Moisture-Cured Polyurethane Sealant Formulation A

Using the same equipment and procedure as in Example 4, a sealant was prepared. A heated water jacket was employed to maintain a batch temperature of 60 °C during and following the incorporation of the modifying additive described below. The same components and quantities as described in Example 4 were used with one exception. Instead of incorporating 930.0 g of BLR/3, the following two items were incorporated at the same stage of manufacture:

#### Example 6: Preparation of One-Component Moisture-Cured Polyurethane Sealant formulation B

Using the same equipment and procedure as in Example 5, a sealant was prepared. The same components and quantities were used but with the following exception. Instead of incorporating 907.5 g of BLR/3 and 22.5 g of the additive from Example 5, the following two items were incorporated at the same stage of manufacture:

40 870.0 g of BLR/3 and 60.0 g of the paste form of rheological additive prepared in Example 2. The finished sealant product was packaged as in Example 5. The tests and results are set forth in Table I. The incorporation of the powdered polyamide or the paste form shown in Table I both provided for excellent control of sag and slump to an otherwise fluid, self-leveling sealant composition. No impairment of 45 extrudability, curability or package stability was observed.

**TABLE I**  
**Sealant Test Results**

	<b>Example</b>	<b>4</b>	<b>5</b>	<b>6</b>
5	Rheological Additive	None	Exempl 1 (powder)	Exempl 2 (paste)
10	Weight Percentage Rheological Additive		1.5	2.0
15	Moisture Curability of Thin (approx 1.25 mm (50 mil) Film)	Cured Through Overnight Non-Tacky	Cured Through Overnight Non-Tacky	Cured Through Overnight Non-Tacky
20	Package Stability	No Appreciable Change in Viscosity or Appearance Upon Ambient Aging for 7 Days	No Appreciable Change in Viscosity or Appearance Upon Ambient Aging For 7 Days	No Appreciable Change in Viscosity or Appearance Upon Ambient Aging For 7 Days
25	RT Flow Rate SAE VIS-2 Castor-Severs Flowmeter 20 grammes, 0.104 in (2.64mm) orifice 276 KPa (40psi) (s) 552 KPa (80 psi) (s)	44 20	99 40	99 39
30	ASTM D2202, Modified Boeing Slump Test 60 Min at RT (mm)	Over 100 (after 30 sec)	0.5	0.5
35	ASTM C639, Modified Vertical Channel Sage Test 60 Min at RT (mm)	Too Fluid To Test	3.8	2.5
40	Bohlin Rheometer System Measuring System: CP 5/30			
45	Torque Element: 289.145 g cm Shear Rate (s <sup>-1</sup> ) 0.1172 14.75	Viscosity* 486.8 165.4	Viscosity* 1471 209.3	Viscosity* 1123 170.4
50	TI = <u>(Pa.s)</u> at 1172s <sup>-1</sup> (Pa.s) at 14.75s <sup>-1</sup>	2.94	7.03	6.59
	*Pa.s			

### Claims

55 1. A polyamide composition prepared by at least one of the following reactions:  
     (1) reacting at least one polycarboxylic acid of the formula (I)  
     (A)[COOH]<sub>x</sub> (I)

wherein x is at least 2 and A is an x-valent aliphatic, aromatic, cycloaliphatic, or arylaliphatic group with  
at least one monoamine of the formula (II)

5 (G)NH (II)

wherein (G) is an aliphatic, aromatic, cycloaliphatic, or arylaliphatic group;  
10 (2) reacting at least one polycarboxylic acid of the formula (I), at least one monoamine of the formula  
(II), and at least one polyamine of the formula (III)

(D)[NH]<sub>y</sub> (III)

wherein y is at least 2 and D is a y-valent aliphatic, aromatic, cycloaliphatic, or arylaliphatic group;  
15 (3) reacting at least one polyamine of the formula (III) with

at least one monocarboxylic acid of the formula (IV)

(E)COOH (IV)

20 wherein E is an aliphatic, aromatic, cycloaliphatic, or arylaliphatic group;  
(4) reacting at least one polycarboxylic acid of the formula (I),

at least one polyamine of the formula (III), and at least one monocarboxylic acid of the formula (IV);

- 25 2. A polyamide composition according to Claim 1 characterized in that said polycarboxylic acid is a dimerized fatty acid, trimerized fatty acid, dicarboxylic acid containing from 6 to 22 carbon atoms, or tricarboxylic acid containing from 6 to 22 carbon atoms.
- 30 3. A polyamide composition according to Claim 1 characterized in that said monocarboxylic acid is a saturated, ethylenically unsaturated or acetylenically unsaturated, naturally occurring or synthetic monobasic aliphatic acid containing from 8 to 24 carbon atoms.
- 35 4. A polyamide composition according to Claim 1 characterized in that said polyamine is an aliphatic, aromatic, primary or secondary diamine containing from 2 to 54 carbon atoms, or an aliphatic, aromatic, primary or secondary triamine containing from 2 to 54 carbon atoms.
- 40 5. A polyamide composition according to Claim 1 characterized in that said monoamine is saturated, ethylenically unsaturated or acetylenically unsaturated, naturally occurring or synthetic, primary or secondary monoamine containing from 8 to 24 carbon atoms.
- 45 6. The polyamide composition according to Claim 1 characterized in that, in reaction (1) said polycarboxylic acid is a dimer acid, trimer acid, sebacic acid, azelaic acid or dodecanedioic acid and said monoamine is octadecylamine, dodecylamine or oleylamine.
- 50 7. A polyamide composition according to claim 6 characterized in that said dimer acid is present in an amount of from 0 to 1.0 moles, and said sebacic acid is present in an amount of from 0 to 0.3 moles and the total moles of dimer acid and sebacic acid equals 1.0 and said octadecylamine is present in an amount of from 1.8 to 2.2 moles.
- 55 8. A polyamide composition comprising products selected from the group consisting of products formed by any of reactions (1) - (4) of claim 1.
9. A rheological additive comprising a polyamide composition according to any one of claims 1 to 8.
10. A sealant composite comprising a polyamide composition according to any one of claims 1 to 8.
11. A caulk composite comprising a polyamide composition according to any one of claims 1 to 8.

12. An adhesive composite comprising a polyamide composition according to any one of claims 1 to 8.
13. A coating composite comprising a polyamide composition according to any one of claims 1 to 8.
- 5 14. A paste composite comprising a polyamide composition according to any one of claims 1 to 8.

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DOCUMENTS CONSIDERED TO BE RELEVANT		Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl.5)		
Category	Citation of document with indication, where appropriate, of relevant passages				
X	DE-A-2 420 955 (BUCKMAN) * Entire document * - - -	1-3,5,6,8, 14	C 07 C 233/08 C 07 C 233/05 C 08 K 5/20 C 09 J 175/08 C 08 L 75/08 C 08 G 18/32 C 09 K 3/10		
X	US-A-3 860 540 (HEINZ et al.) * Examples 36,38,43a * - - -	1,2,4,8,14			
X	US-A-3 219 612 (SKAU et al.) * Examples 17,19,28,30 * - - -	1,2,3,4,5, 8,14			
X	US-A-2 965 591 (DAZZI) * Example 1; column 3, lines 27-30 * - - -	1,2,5,8,14			
X	US-A-2 992 145 (SANTANGELO) * Preparation F * - - -	1,2,4,8,14			
X	US-A-3 256 182 (SCHERER) * Claim 1; column 8, lines 18-49 * - - -	1-4,8-14			
X	US-A-2 594 286 (BRYANT et al.) - - -	1,2,5-9, 13,14			
X	DERWENT WPIL ONLINE ABSTRACT, accession no. 88-060442 [09], Derwent Publications Ltd, London, GB; & JP-A-63 015 876 (MITSUI TOATSU) * Abstract * - - -	1,3,4, 8-14	TECHNICAL FIELDS SEARCHED (Int. Cl.5)		
X	EP-A-0 195 218 (HENKEL) * Page 12, table 1, polyamid C * - - -	1,2,4, 8-12	C 07 C 233/00 C 08 K 5/00 C 09 K 3/00 C 11 C 3/00		
X	GB-A-1 461 355 (COATES) - - -	1,2,3,4, 8-14			
		-/-			
The present search report has been drawn up for all claims					
Place of search	Date of completion of search	Examiner			
The Hague	18 October 91	WELLS A.G.			
CATEGORICAL OF CITED DOCUMENTS					
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P: intermediate document	.....				
T: theory or principle underlying the invention	&: member of the same patent family, corresponding document				

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## DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl.5)
X	EP-A-0 277 420 (N.L. CHEMICALS) - - -	1,2,3,4,8, 9,13	
X	CHEMICAL ABSTRACTS, vol. 109, 1988, page 539, abstract no. 14596e, Columbus, Ohio, US; & JP-A-62 212 650 (MITSUBISHI PAPER MILLS, LTD) 18-09-1987 * Abstract * & GENERIC DARC ONLINE GRAPHIC OF CHEMICAL ABSTRACTS registry no. 114896-35-4 - - -	1,2,3,5,8, 9,13	
X	CHEMICAL ABSTRACTS, vol. 102, 1985, page 43, abstract no. 46829e, Columbus, Ohio, US; & JP-A-59 161 441 (HITACHI CHEMICAL CO., LTD) 12-01-1984 * Abstract * & GENERIC DARC ONLINE GRAPHIC OF CHEMICAL ABSTRACTS, registry no. 35081-84-6 - - -	1,2,3,5,6, 7,8-14	
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X	CHEMICAL ABSTRACTS, vol. 104, 1986, page 289, abstract no. 73486p, Columbus, Ohio, US; & JP-A-60 170 594 (NIHON GENMA K.K.) 04-09-1985 * Abstract * & GENERIC DARC ONLINE GRAPHIC OF CHEMICAL ABSTRACTS, registry no. 88815-30-9 - - -	1-3,5-9, 14	TECHNICAL FIELDS SEARCHED (Int. Cl.5)
		-/-	

The present search report has been drawn up for all claims

Place of search	Date of completion of search	Examiner
The Hague	18 October 91	WELLS A.G.

## CATEGORY OF CITED DOCUMENTS

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DOCUMENTS CONSIDERED TO BE RELEVANT		Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl.5)		
Category	Citation of document with indication, where appropriate, of relevant passages				
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X	CHEMICAL ABSTRACTS, vol. 61, 1964, abstract no. 4209f, Columbus, Ohio, US; N. WADA et al.: "Rust preventive effect of dibasic acid alkylamides", & OSAKA FURITSU KOGYO-SHOREIKAN HOKUKU No. 26, 58-62(1961) * Abstract; in particular N,N'-dilaurylsebacamide * - - -	1,2,3,5-8, 14			
X	CHEMICAL ABSTRACTS, vol. 86, 1977, page 45, abstract no. 30695y, Columbus, Ohio, US; & JP-A-76 114 482 (CHISSO CORP.) 08-10-1976 * Abstract; in particular N,N'-dioctadecylnonanediameide * - - -	1,2,3,5,6, 8,12,13			
		TECHNICAL FIELDS SEARCHED (Int. Cl.5)			
The present search report has been drawn up for all claims					
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